

Instrumental Technique

Temperature Program Desorption

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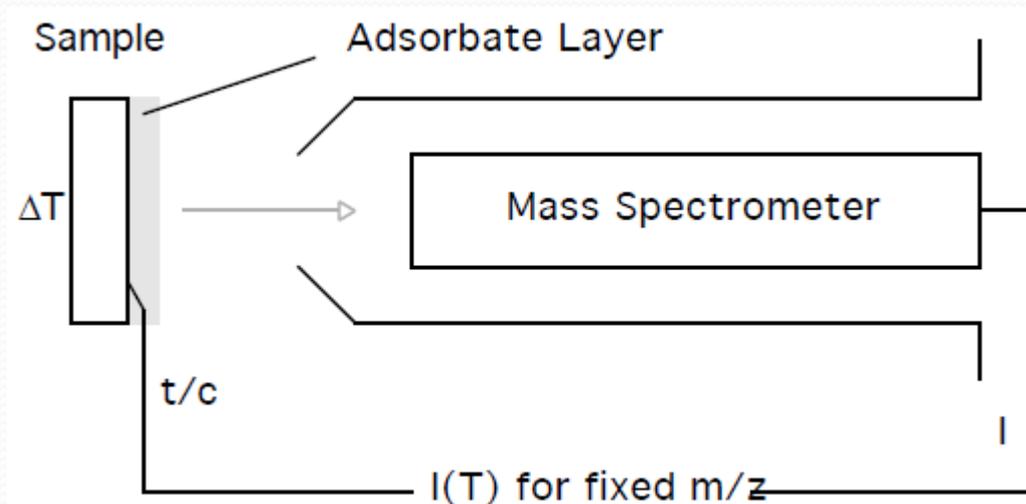
Temperature Programmed Desorption (TPD):

..... also known as thermal desorption spectroscopy (TDS)

In TPD experiment, gaseous molecule/atom is adsorbed onto surface (sometimes cooled) then desorbed by heating surface

General setup:

- Adsorb/deposit fixed amount of molecules at surface
- Gradually increased heating of surface leads to desorption
- Desorbed particles analyzed by pressure gauge/mass spectrometer



Information on:

-Heat of adsorption (if adsorption and desorption are reversible/nondissociative processes)

-Quantitative coverage information about dissociative and non-dissociative adsorption

- Energetic information about phases transitions, interadsorbate interactions, multiple adsorption sites

-Kinetic information about desorption process

-Surface reactions (TPRS)

for (a) $E_{\text{ads}} = E_{\text{des}}$ and for (b) $E_{\text{ads}} < E_{\text{des}}$!

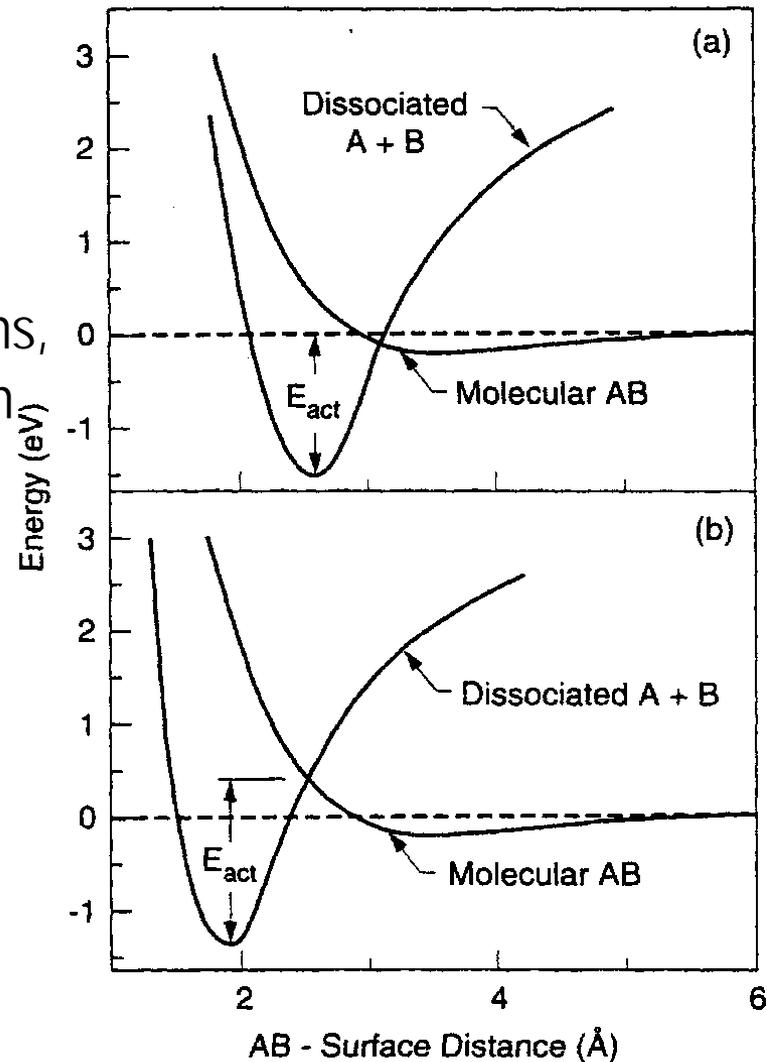


Fig. 3. Conventional Lennard-Jones picture of dissociative adsorption of a diatomic molecule AB on a surface: (a) non-activated; (b) activated.

Two ways to collect data:

(a) thermal desorption (TPD/TDS)

- slow (linear) temperature ramp (few K/s)
- rate of desorption < pumping speed of vacuum system (negligible re)

adsorption from gas phase: UHV)

- most common method

(b) flash desorption

- rate of desorption > pumping speed of vacuum system
- rarely used
- primarily used for surface cleaning

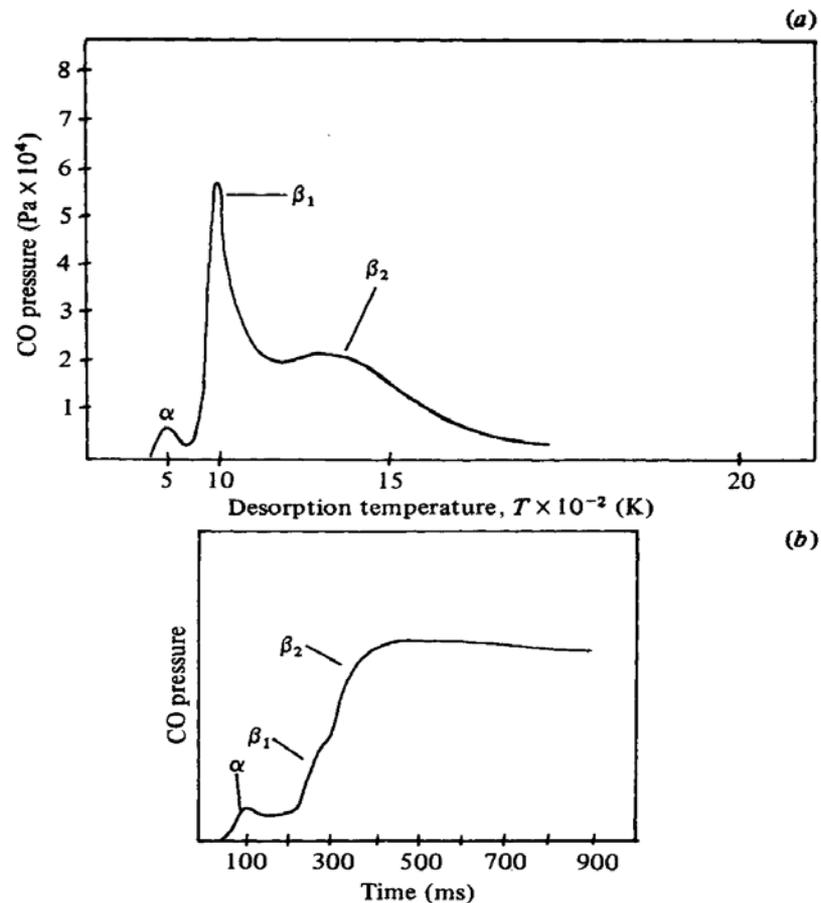


Fig. 5.1 Comparison of (a) thermal desorption and (b) flash desorption curves showing the α , β_1 and β_2 states of CO on W (Goymour & King, 1973; Ehrlich, 1961b).

Partial pressure recorded at one m/z (say, base peak) by mass spectrometer is

- \propto to instantaneous partial pressure of adsorbate θ_M
- \propto to rate of desorption of adsorbate dM/dt
- $dM/dt =$ rate of loss of coverage $-d\theta_M/dt$

Several points worth noting:

- $I(T)$ does not rise indefinitely - at some stage, all molecules desorbed
- If the mass spectrometer collected and ionized all adsorbates, area under TPD $I(T)$ curve would *equal* molecular coverage
- Only fraction desorbed molecules collected and ionized – area under TPD $I(T)$ curve is *proportional* to molecular coverage
- Shape of $I(T)$ curve contains information about desorption kinetics

The rate of desorption follows Arrhenius-type behavior

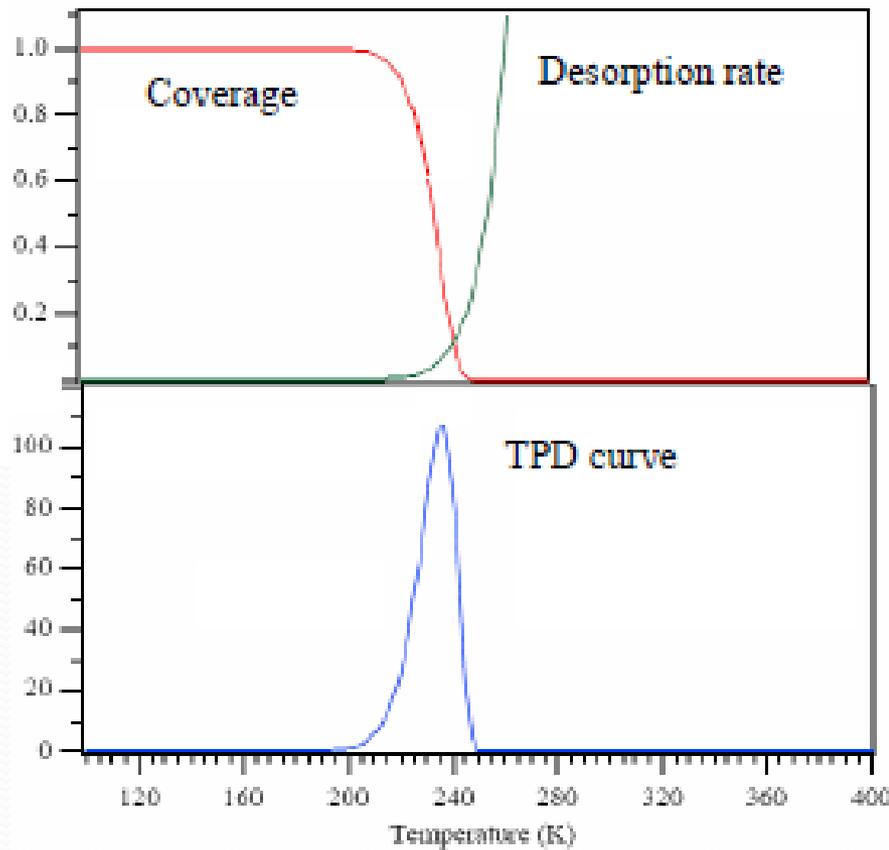
$$I(T) \propto \frac{dM}{dt} = -\frac{d\theta_M}{dt} = \nu(\theta_M) \cdot \theta_M^n \cdot \exp\left(\frac{-E_{des}(\theta_M)}{R \cdot T}\right)$$

Number of desorbing particles depends on rate of desorption: increases monotonously with T
 number of adsorbed particles: decreases monotonously with T

where

- $\nu(\theta_M)$ = frequency factor
- θ_M = instantaneous coverage
- n = kinetic order or desorption order
- $E_{des}(\theta_M)$ = activation energy to desorption
- R = gas constant

- In general:
- E_{des} larger → peak shifts to higher T
- ν smaller → peak shifts to higher T
- Faster heating rate → peak shifts slightly to higher T desorption



Significance of Desorption Order (n):

Most terms in Polanyi-Wigner equation straightforward

Factors affecting peak desorption temperature: - E_{des} , ν , β , θ_M ($n \neq 1$)

Factors affecting peak shape: - ν , β , n

Factors affecting peak magnitude (area): - θ_M

Zero-order kinetics:

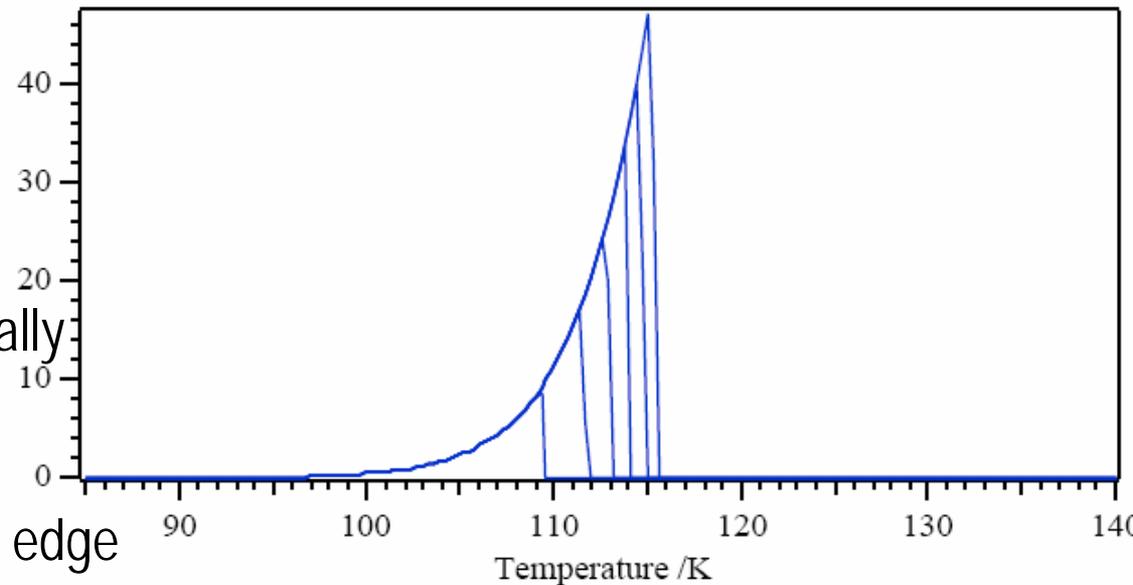
-desorption rate does not depend on coverage

-desorption rate increases exponentially with T

-all coverages have common leading edge

-rapid drop when all molecules have desorbed

-temperature of peak desorption rate, T_m , moves to higher T with θ_M



First-order kinetics:

-desorption rate proportional to

low balance
terms
ing qm
ic peak

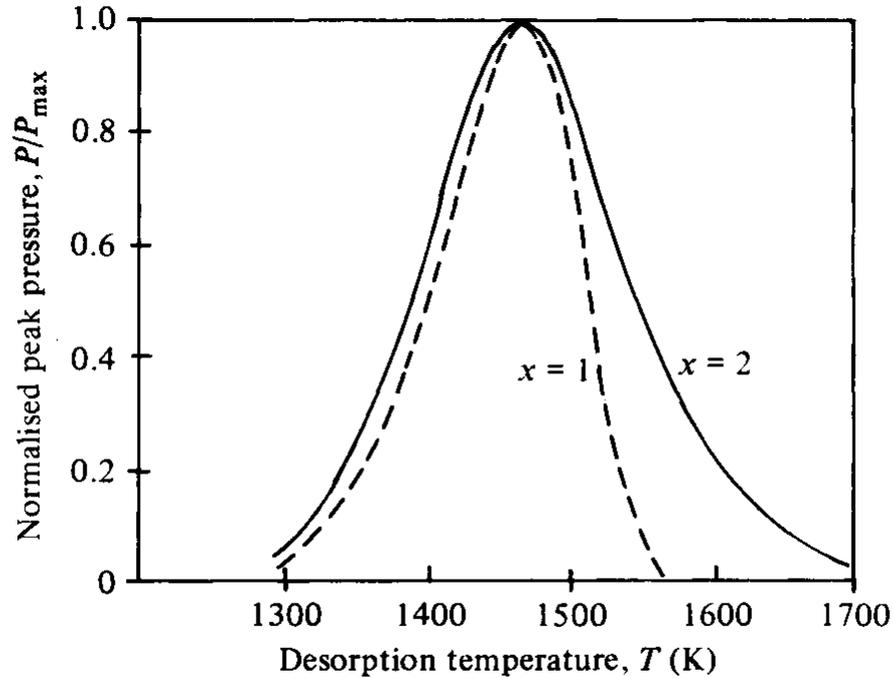
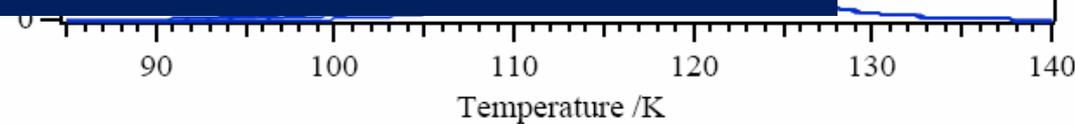


Fig. 5.6 The theoretical shapes of first- and second-order desorption peaks (Redhead, 1962).

Second-

-desorption
instantaneous
-desorption
balance
terms
T_m move

- Common trailing edges of peaks
- Characteristic nearly symmetric peak shape



Summary:

- Simple, rapid
- Quantitative coverage information (simplest case)
- Can accurately determine exposure required for 1 ML coverage (in layer-by-layer systems)
- Provides information about adsorption/desorption enthalpies (simplest non-dissociative case)
- Provides information about layer stability
- Provides information about fragmentation and reaction in dissociative adsorption (TPR)

BUT:

- Destructive
- Binding sites occupied at low temperature not necessarily those from which molecule desorbs during TPD
- Mathematical treatment of data useful but can be easily misapplied
- Often very complex desorption kinetics observed even for simple systems
 - ν , E_{des} , n are temperature dependant
- Difficult to determine temperature of reaction
- Fragments with coincident m/z peaks can complicate interpretation

Analysis of TPD Data:

Polanyi-Wigner equation can be rewritten

$$-\frac{d\theta_M}{dt} = v \cdot \theta_M^n \cdot \exp\left(\frac{-E_{des}}{R \cdot T}\right)$$

$$\ln\left(\frac{d\theta_M}{dt}\right) = \ln v + n \cdot \ln\theta_M + \frac{-E_{des}}{R \cdot T}$$

A graph of $\ln\left(\frac{d\theta_M}{dt}\right)$ versus $\frac{1}{T}$ will produce a straight line of slope $\frac{-E_{des}}{R}$ and intercept $\ln v + n \cdot \ln\theta_M$

- if the correct value of n (order) is chosen
- if E_{des} and n are coverage independent
- Arrhenius plot

Usually, first part of desorption trace used (<5 % desorption) where θ_M doesn't change appreciably ("leading edge" analysis)

Example of TPD Data: CO₂ on NaCl(100)

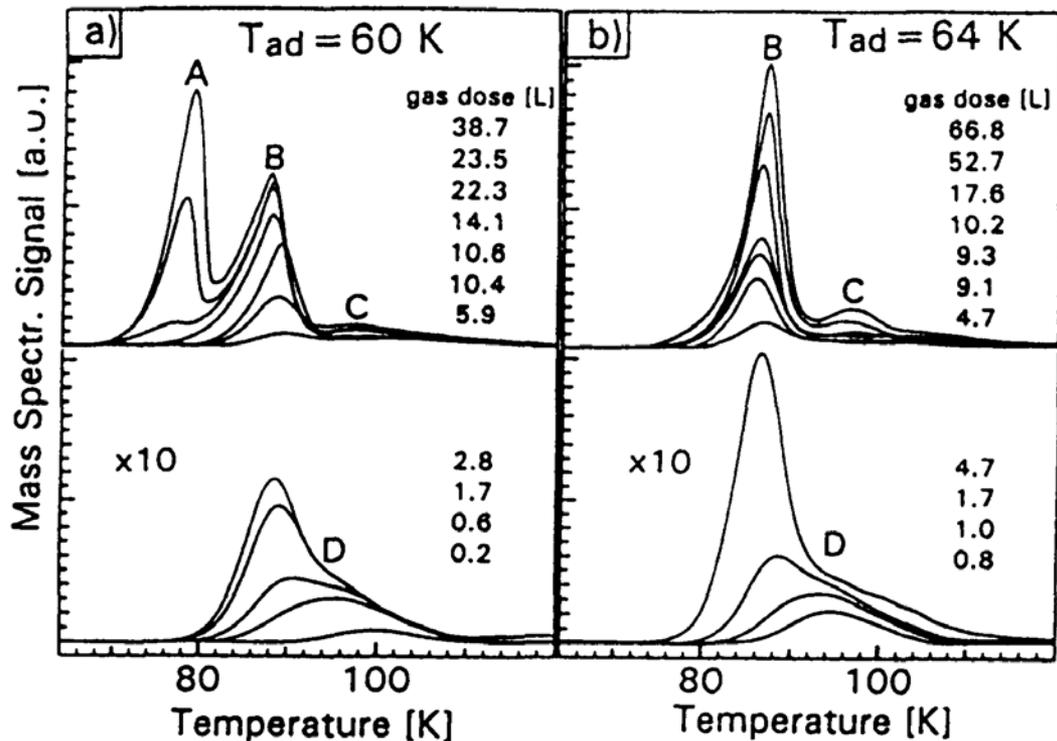


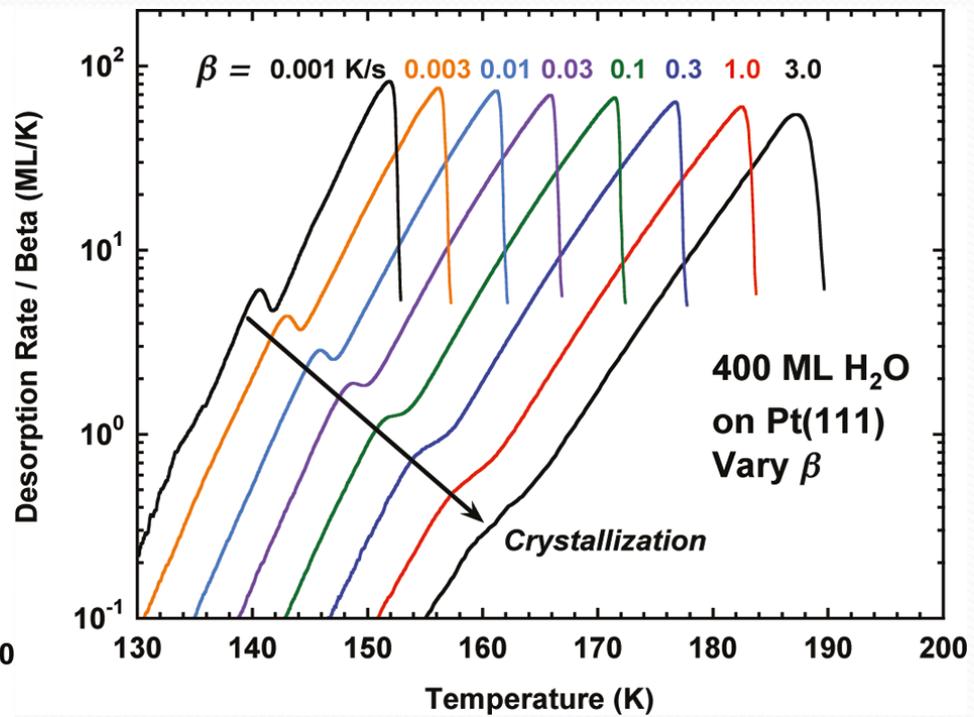
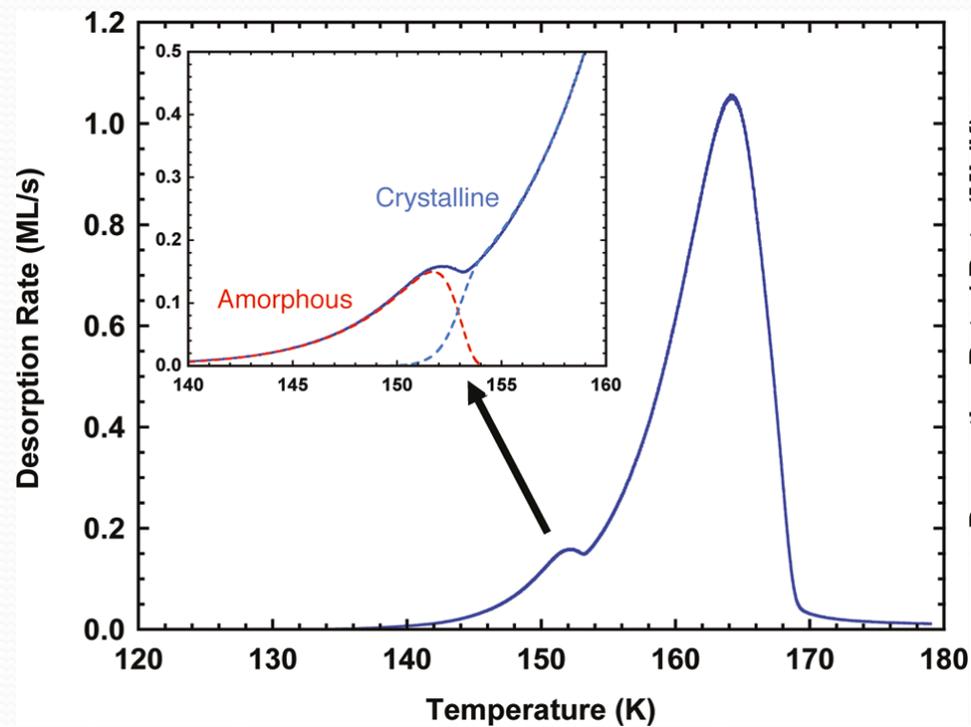
Fig. 3a, left: TPD spectra of CO₂ after adsorption on NaCl(100) at 60 K. Fig. 3b, right: TPD spectra of CO₂ after adsorption at 64 K. The relative quantities are given as exposures (in Langmuir; 15 L correspond approximately to a monolayer).

Even for simple adsorbates, often complex desorption behavior. Four peaks visible

- A - multilayer ($E_{des} \sim 21 \text{ kJ}\cdot\text{mol}^{-1}$)
- B - monolayer ($E_{des} \sim 26 \text{ kJ}\cdot\text{mol}^{-1}$)
- C - artifact (desorption from sample holder)
- D - defects and step-edges

Different layer morphology when adsorbed at 60 K or 64 K

- 60 K - separate monolayer/multilayer
- 64 K - one peak that does not saturate (islanding?)



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Thank You